

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-127683

(43)Date of publication of application : 16.05.1997

(51)Int.Cl.

G03F 7/00

B41M 1/06

(21)Application number : 07-283247

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(22)Date of filing : 31.10.1995

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## (54) PLANOGRAPHIC PRINTING PLATE AND PRINTING METHOD

## (57)Abstract:

PROBLEM TO BE SOLVED: To enable direct plate making according to signals from a computer, to obtain high resolution and high stability for deposition of an ink in an image part, and to decrease contamination in a nonimage part with an ink by forming a layer of specified self-water dispersible thermoplastic resin particles on the surface of a hydrophilic substrate.

SOLUTION: The layer of self water dispersible thermoplastic resin particles which can be changed into oleophilic by heat is formed on the surface of a hydrophilic substrate, preferably an aluminum plate. In this case, the resin for the self-water dispersible thermoplastic resin particles is not limited and the resin is preferably a copolymer containing a monomer unit selected from styrene, substd. styrene such as  $\alpha$ -styrene, acrylates such as methylacrylate and 2-ethylhexyl acrylate, and methacrylates such as methylmethacrylate and 2-ethylhexyl methacrylate, and a monomer unit selected from acrylic acids and methacrylic acids.

## LEGAL STATUS

[Date of request for examination] 26.11.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3555668

[Date of registration] 21.05.2004

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

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[Claim(s)]

[Claim 1] the base front face of a hydrophilic property — heat — lipophilic — the lithography plate characterized by forming the self-water-dispersion thermoplastics particle layer [-izing / the layer ].

[Claim 2] The lithography plate according to claim 1 characterized by the base of a hydrophilic property being an aluminum plate.

[Claim 3] The lithography plate according to claim 1 or 2 with which self-water-dispersion thermoplastics is characterized by being resin with which it comes to neutralize the acid number or more 50 some 280 or less synthetic resin [ at least ] (A) by the base (B).

[Claim 4] The lithography plate according to claim 3 whose glass transition temperature of synthetic resin (A) is 50 degrees C or more.

[Claim 5] The lithography plate according to claim 3 or 4 characterized by being self-water-dispersion resin with which more than 60 mol % of the acid radical of synthetic resin (A) is neutralized by the base (B).

[Claim 6] The lithography plate according to claim 3, 4, or 5 which is the copolymer of at least one monomer chosen from the group which synthetic resin (A) becomes from styrene, permutation styrene, and acrylic ester (meta), and acrylic acid (meta).

[Claim 7] The lithography plate according to claim 3, 4, or 5 characterized by self-water-dispersion thermoplastics being ionomer resin (I) of the structure in which a part of functional-group whole quantity [ at least ] which gives the acid number in synthetic resin (A) carried out intermolecular bridge formation, and which it unified through polyvalent metal ion (C).

[Claim 8] The lithography plate according to claim 3, 4, 5, 6, or 7 whose base (B) is an alcoholic amine.

[Claim 9] The lithography plate according to claim 8 whose base (B) is triethanolamine.

[Claim 10] The lithography plate according to claim 1 or 2 which contains a particle abherent (D) in a self-water-dispersion thermoplastics particle layer.

[Claim 11] The lithography plate according to claim 10 characterized by a particle abherent (D) being polyhydric alcohol.

[Claim 12] The lithography plate according to claim 11 characterized by a particle abherent (D) being a glycerol.

[Claim 13] The lithography plate according to claim 8, 9, 11, or 12 characterized by forming the film for desiccation prevention which can further exfoliate on the self-water-dispersion thermoplastics particle layer on the base front face of a hydrophilic property.

[Claim 14] the base front face of a hydrophilic property — heat — lipophilic — the printing approach characterize by to print by give heat energy to the lithography plate with which the self-water-dispersion thermoplastics particle layer [-izing / a layer ] be form, make said particle of a desired location lipophilic to it, make a thermal melting arrival image form in it, dip in it, impress ink on said thermal melting arrival image using water, and imprint it on the record body.

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the lithography version which can be printed as it is, without forming in detail the image section which can impress ink alternatively by carrying out direct writing with the laser light in heat mode, and performing development actuation about the printing version for lithography.

[0002]

[Description of the Prior Art] The conventional platemaking system engraved [ which time and effort requires very much ] by creating the film of a negative or a positive from the block copy, being burned on PS plate which applied photosensitive polymer, and developing negatives further. Digitization of platemaking progresses quickly in recent years, and the means which connects the electrical signal from a computer to direct platemaking is proposed.

[0003] Although the approach of developing and platemaking-izing is common after changing the electrical signal from a computer into laser light and specifically being burned on photosensitive polymer, a development process is still required. Moreover, although it considers as the approach of carrying out the material transfer of the image formation ingredient, and engraving on the direct version and ink jet record and an electrophotography method are proposed, it has the fault in the reappearance stability and resolution of the image section.

[0004] Although the original edition for straight-writing mold offset printing which uses the microencapsulated lipophilic matter as an image acceptance layer, destroys a microcapsule layer by the printer of an impact method, and forms the image section is proposed by JP,62-1587,A as the other approaches. The particle diameter of a microcapsule is large and it has the fault of the breadth of the image section not being avoided in order to destroy a capsule by the impact, but the resolution of the printed matter obtained being fundamentally low, and being further easy to produce the printing dirt by destruction of the capsule of the non-image section on a version.

[0005] The direct platemaking which engraves without attaining the reappearance stability and high resolution of a printing image, and performing development actuation using a thermal head and laser light as a means is proposed variously. for example , although it be the approach of carry out chemical conversion of the front face of the body which use oleophilic resin as a component , form a hydrophilic layer , and laser light remove that hydrophilic layer alternatively , and make the image section form , by this approach , JP,49-118501,A consume energy seriously , and its platemaking rate be also slow and it have the fault that resolution be low , for generating of polymer waste or a cinder .

[0006] although JP,51-63704,A change by irradiate the plate a plate be covered by the hydrophilic polymer layer which consist of a nonphotosensitivity compound with laser light so that an exposure part harden , it become hydrophobicity or oleophilic and ink be absorb , it be difficult JP,51-63704,A to change the image section to a homogeneity firmly , and it have the fault of the water-soluble polymer which constitute the non-image section during printing be elute , and be easy to generate printing dirt , by this approach .

[0007] Although the method of applying to a base material the thermofusion matter microencapsulated with the pigment in the thermofusion matter, changing a heating unit to oleophilic, and impressing ink is proposed in JP,3-108588,A, it has the fault of being easy to produce printing dirt the resolution of the printed matter with which the particle diameter of a microcapsule is obtained greatly being fundamentally low, and the oleophilic thermofusion matter tending to adhere to a base material through destruction and the wall of a capsule on a version.

[0008] Although it was the approach of JP,6-71787,B introducing a sulfonic acid group into the front face of the plate which consists of an oleophilic polymer, and forming the non-image section, and removing a surface sulfonic acid group alternatively by the exposure of the laser light which has specific energy density, and forming the image section, it had the fault of being easy to produce printing dirt, by partial exposure of the oleophilic polymer layer of the surface lower part carried out in sulfonic acid group processing.

[0009] It consists of the hydrophilic layers and base materials containing the microencapsulated oleophilic component which is converted into the image section with heat in JP,7-1849,A and JP,7-1850,A, and a hydrophilic binder polymer. Although the sensible-heat lithography version devised so that three-dimensions bridge formation of the hydrophilic binder polymer might be carried out and a capsule might carry out an after [ destruction ] chemical bond to the lipophilic component in a microcapsule is proposed. Fundamentally low and fundamentally, since the boundary of a lipophilic component and a hydrophilic polymer is not clear, the resolution of the printed matter with which the particle diameter of a microcapsule is obtained greatly fully [ the adhesion of a hydrophilic polymer and a base material ] has the problem of the fall of printing dirt or resolution.

[0010]

[Problem(s) to be Solved by the Invention] The technical problem which this invention tends to solve is to offer the printing approach in which direct platemaking of the signal from a computer is possible, and the lithography plate which is excellent in the ink impression stability in the image section with high resolution, and does not have ink dirt of the non-image section and stable printing are possible.

[0011]

[Means for Solving the Problem] this invention person etc. came to solve this invention, as a result of repeating research wholeheartedly, in order to solve the above-mentioned technical problem.

[0012] namely, this invention — the base front face of a hydrophilic property, and the heat preferably formed in the aluminum plate front face — lipophilic — the lithography plate with which the self-water-dispersion thermoplastics particle layer [—izing / the layer] is formed and which can be engraved direct is offered.

[0013] moreover, the base front face of a hydrophilic property — heat — lipophilic — the printing approach characterize by to print by give heat energy to the lithography plate with which the self-water-dispersion thermoplastics particle layer [—izing / a layer] be form, make said particle of a desired location lipophilic to it, make a thermal melting arrival image form in it, dip in it, impress ink on said thermal melting arrival image using water, and imprint it on the record body offer.

[0014] The acid number the self-water-dispersion thermoplastics of said lithography plate 280 or less [ 50 or more ] The self-water-dispersion resin with which it comes to neutralize glass transition temperature some synthetic resin [ at least ] (A) 50 degrees C or more by bases (B), such as an alcoholic amine, preferably, The lithography plate which is ionomer resin (I) of the structure in which a part of functional-group whole quantity [ at least ] which gives the acid number of synthetic resin (A) preferably especially carried out intermolecular bridge formation, and which it unified through polyvalent metal ion (C) is offered.

[0015] Particle abherents (D), such as polyhydric alcohol, are contained in the self-water-dispersion thermoplastics particle layer of said lithography plate, and the lithography plate with which the film for the still more desirable desiccation prevention which can exfoliate on the self-water-dispersion thermoplastics particle layer on the base front face of a hydrophilic property is formed is offered.

[0016] The printing plate of this invention is used for the so-called lithography which has the self-water-dispersion thermoplastics particle layer formed in the base front face, adds energy to a printing plate alternatively, gives inking to a welding resin particle layer for this resin particle welding and after making it lipophilic, imprints ink on the recorded body further, and forms a printing image.

[0017] If a self-water-dispersion thermoplastics particle can be alternatively welded by exposure as an energy gestalt given to a printing plate, although there is especially no limit, its heat energy is simple and is efficient, and although there are a thermal head, laser light, etc. as a heat source, the laser light in which direct writing is possible is the most desirable in a detailed pattern non-contact. In respect of resolution, the particle diameter of this resin particle is so good that it is small, and its 0.1 micrometers or less are still more preferably desirable 1 micrometer or less.

[0018] On the other hand, the non-drawn part of a printing plate is rich in the hydrophilic property, by grant of remaining as it is or dampening water, can prevent impression of printing ink and can make it the non-image section. If printing furthermore progresses, it will secede from the self-water-dispersion thermoplastics particle of non-welding easily from a base front face, and the same printing stability as the conventional lithography plate will be acquired according to the hydrophilic effectiveness of base original.

[0019] Since a version is beforehand developed using water etc. and this resin particle of the non-image section is removed in advance if needed, you may make it use, although the development actuation in platemaking will become unnecessary if the printing plate of this invention is used as mentioned above.

[0020] The purpose of the lithography plate of this invention is making easy balking from the base of the antisticking, hydrophilic maintenance, and the resin particle of the resin particles of adhesion and ink oilproof with the resolution and the base of the thermofusion image section of a self-water-dispersion thermoplastics particle layer, and the non-melting non-image section.

[0021] It is characterized by forming the self-water-dispersion thermoplastics particle layer [—izing / the layer]. namely, the lithography plate of this invention — the base front face of a hydrophilic property — heat — lipophilic — The paper by which coating processing was carried out although limitation, such as paper, plastics, and a metal, did not have the hydrophilic radical object, the sheet plastic hydrophilic-property-ized by processing of corona discharge etc. in the front face — it is preferably desirable the aluminum plate and that surface treatment, such as graining and anodizing, is performed for the front face still more preferably.

[0022] By the general resin particle, although the self-water-dispersion thermoplastics particle layer on the front face of a base carries out spreading desiccation of the water dispersion of this resin particle on a base front face and is obtained, in order that particles may unite partially and they may form a coat, the hydrophilic property of the non-welding part of laser light becomes inadequate, and balking of the resin particle layer from a base front face is not performed further, but impression of the ink to the non-image section becomes easy to produce the dry paint film.

[0023] Although there are some which have as a substituent the salt of the synthetic resin and the alkali which have the acid number as self-water-dispersion resin, and hydrophilic groups, such as a hydroxyl group In order to give [ and ] a big hydrophilic property to a particle, preventing atomization of a water-dispersion resin particle, and the dissolution and swelling of a particle, it is desirable that the acid number is self-water-dispersion resin with which it

comes to neutralize or more 50 some 280 or less synthetic resin [ at least ] (A) by the base (B) as resin. In order to prevent fusion of these resin particles especially, 50 degrees C or more are [ the glass transition temperature of resin ] desirable still more desirable, and the glass transition temperature of 70 degrees C or more is good.

[0024] In order to make the particle diameter of a resin particle small in order to raise the definition of the image section, to raise the hydrophilic property of the resin particle of the non-welding of the non-image section and to make the ink dirt of the non-image section small, it is desirable that more than 60 mol % of the acid radical of synthetic resin (A) is neutralized by the base (B). Although especially the anionic functional group that gives the acid number to synthetic resin is not limited [ radical / a carboxyl group, a sulfonic group, / sulfinic-acid ], a carboxyl group gives a general and good self-water-dispersion thermoplastics particle.

[0025] Although especially a limit does not have the class of resin of a self-water-dispersion resin particle, as what satisfies particle-izing of resin, the film strength of the image section, the hydrophilic property of the non-image section, etc. Acrylic ester, such as styrene or permutation styrene like alpha methyl styrene, acrylic-acid methyl ester, ethyl-acrylate ester, butyl acrylate ester, and 2-ethylhexyl acrylate ester, At least one or more monomeric units chosen from methacrylic ester, such as methacrylic acid methylester, ethyl methacrylate ester, methacrylic-acid butyl ester, and 2-ethylhexyl methacrylate, A copolymer including at least one or more monomeric units chosen from an acrylic acid and a methacrylic acid is desirable, and although there is especially no limit about the molecular weight range of resin, the thing of or more 1000 100,000 or less molecular weight is more desirable.

[0026] It is desirable that self-water-dispersion thermoplastics is ionomer resin (I) of the structure in which a part of functional-group whole quantity [ at least ] which gives the acid number in synthetic resin (A) carried out intermolecular bridge formation and which it unified through polyvalent metal ion (C) as a means to improve further welding prevention of the particles of the adhesion on the front face of a base of said resin, the abrasion resistance, oilproof and the alkali resistance of the image section, and the non-image section.

[0027] Ionomer resin is chelating resin by association like ion of the polyvalent metal ion which forms the reversible gel which has the network structure which consists of reversible bridge formation unlike the covalent-bond nature bridge formation which forms permanent gel with the permanent network structure, and an anionic radical, the resin particle and thermal melting arrival resin coat which are obtained from this water dispersion are very tough, it is rich in elasticity, and adhesion with a base aluminum plate is excellent. Since reversible bridge formation, i.e., ionic bond energy, is small as compared with covalent-bond energy, even if the rate of bridge formation is high, I hear that good thermoplasticity is shown and it is.

[0028] With [ the valence of the polyvalent metal ion used for ionomer resin ] two [ or more ], anything is sufficient, but it is 2 or 3 preferably and the resin particle obtained from what was especially chosen from calcium ion, barium ion, magnesium ion, zinc ion, and aluminum ion at least one or more preferably is colorlessness, there is also little toxicity and good tough and good thermoplasticity is shown. The ionomer resin water dispersion by which gelation of synthetic resin was stabilized few is obtained, and bridge formation of the resin by these polyvalent metal ion also has few falls of the heat flow rate dynamic characteristics of a resin particle, when a bridge is constructed with the polyvalent metal ion of the amount which corresponds to 30% from 1% of a desirable anionic functional group.

[0029] As for polyvalent metal ion, what is added by the resin solution as a metal or fusibility polyvalent metallic salt, and is chosen from the metal chelate of ligands, such as carboxylate of polyvalent metal, and an acetylacetone, an acetoacetic ester salt, and polyvalent metal is desirable in respect of the solubility over the ease of carrying out and organic solvent of acquisition.

[0030] Although the solubility of resin will fall according to bridge formation and gelation and diameter-ization of a large drop of a resin emulsification object will arise if these fusibility metal salt is put into a synthetic-resin solution, by raising solution temperature at this time, or adding superfluously an volatile chelating agent like an acetylacetone or acetoacetic ester, gelation is prevented and the resin emulsification object of the diameter of a particle is obtained.

[0031] The base (B) for giving self-water-dispersion to said synthetic resin (A) has big effect on oleophilic [ of the thermal melting arrival by the hydrophilic property of this resin particle, and laser light exposure, and a welding resin coat ]. If lipophilic-izing of the thermal melting arrival coat by laser light exposure is not enough, ink impression of the image section is inadequate, when a base (B) is alkali metal, and volatility is too high like ammonia, although ink impression of the image section is enough, this resin particle of the non-image section will make it lipophilic, and it will tend to produce the ink dirt of a version. amines with vapor pressure low as a desirable base (B) — desirable — an alcoholic amine — triethanolamine is still more preferably desirable.

[0032] In this invention, in order to prevent the ink dirt of a version further Particle adherents, such as water soluble resin, a hydrophilic inorganic particle particle, and polyhydric alcohol, can be included in a self-water-dispersion thermoplastics particle layer. When polyhydric alcohol, especially polyhydric alcohol are glycerols preferably, even if the resin particle remains on the base front face, the ink impression to the non-image section is prevented effectively. And balking of the resin particle from a hydrophilic radical body surface is made easy, and ink dirt prevention of the conventional printing plate and the version more than an EQC is attained.

[0033] When said liquefied base and particle adherent are included in the self-water-dispersion thermoplastics particle layer on the base front face of a hydrophilic property, it is desirable to form the film for desiccation prevention which can exfoliate in order to raise the preservation stability of a version on this resin particle layer.

[0034] Unlike what emulsified compulsorily a known emulsion-polymerization method and a known oleophilic polymer with the emulsifier, the self-water-dispersion thermoplastics particle of this invention is obtained by the phase inversion emulsifying method for the ability to obtain easily the self-emulsifiability resin particle which essentially

has a hydrophilic property.

[0035] After dissolving self-water-dispersion resin in an organic solvent as a first stage story, specifically, the neutralization base of the specified quantity is mixed further. It emulsifies by making the resin solution obtained on the first stage story mix the aqueous medium of an excessive amount as a second stage story, and the water dispersion of a resin particle is obtained.

[0036] In order to raise the distributed stability of resin particle dispersion liquid as the third step if needed, the deliquoring process which removes the organic solvent used on the first stage story may be put in. Moreover, after the second or the process of the third step is completed, it is desirable to perform the process which removes the diameter resin particle of a large drop by filter filtration, centrifugal separation, etc.

[0037] the organic solvent which is alike in a first stage story and dissolves synthetic resin (A) — ketone solvent, such as an acetone, dimethyl ketone, and a methyl ethyl ketone, — Alcoholic solvent, such as a methanol, ethanol, and isopropyl alcohol, Aromatic series system solvents, such as chlorine-based solvents, such as chloroform and a methylene chloride, benzene, and toluene, Although it is usable if resin, such as glycol ether system solvents, such as ester solvent, such as ethyl-acetate ester, ethylene glycol monomethyl ether, and ethylene glycol wood ether, and amides, is dissolved When a resinous principle is acrylic resin, at least one or more kinds of combination chosen from ketone solvent and alcoholic solvent is good.

[0038] Although the amount of this organic solvent used will not be specified especially if the effectiveness in this invention is attained, its amount from which the weight ratio of synthetic resin / this organic solvent is set to 1 / 1 — 1/20 is desirable.

[0039] A dispersant, a plasticizer, an antioxidant, an ultraviolet ray absorbent, the energy-absorbing agent for absorbing the energy to irradiate efficiently, etc. can also be added to the above-mentioned synthetic-resin solution as an additive if needed.

[0040] The aqueous medium mixed with the above-mentioned synthetic-resin solution has desirable water of the grade more than ion exchange water, in order to avoid the effect by impurity or heavy metal.

[0041] Moreover, although it is desirable in a self-water-dispersion resin particle layer to use a particle adherent (D) together, there are inorganic particles, such as polyhydric alcohol, such as ethylene glycol, a diethylene glycol, a polyethylene glycol, and a glycerol, and colloidal silica, a surfactant, etc. in it as a particle adherent (D) and it is not limited to these, in especially this invention, a glycerol is effective for welding prevention of particles.

[0042] Although these particles adherent (D) may be added into said aqueous medium used for emulsification about a liquefied thing, adding after mixing may be carried out to the water dispersion of this resin particle, and those additions are usually in the range of the 1 — 500 weight section to this resin particle 100 weight section.

[0043] The obtained self-water-dispersion resin particle distribution solution removes spreading, superfluous water, and the organic solvent of a low-boiling point by the known approach on hydrophilic radical objects, such as aluminum, and uses them as a printing plate. Not each particle of the obtained self-water-dispersion resin particle layer changes appearance to the usual resin layer, without seceding easily from on a printing plate unlike the so-called fine-particles particle. In a self-water-dispersion resin particle solution, said particle adhesion agent, antiseptics, the particle cross linking agent that can be activated by laser light may be added as an additive.

[0044] In saving a prolonged printing plate, in order to prevent adhesion of the particles accompanying evaporation of these solvents and to protect a printing plate by the case where a solvent like a glycerol as an alcoholic amine and a particle adherent is used as a base, covering with the film of PET etc. which can be exfoliated is desirable.

[0045] as the laser light source used for the platemaking of the lithography plate of this invention, a temperature up is possible to the temperature which self-water-dispersion resin particles weld, and there are specifically semiconductor laser (oscillation wavelength of 780nm / 840nm), carbon dioxide laser (said — 10.6 micrometers), an YAG laser (said — 532.1060nm), an excimer laser (said — 193\*\*308\*\*351 nm) argon laser (said — 488nm), etc. that what is necessary is to just be controlled by extent which the etching of a self-water-dispersion resin particle layer does not produce.

[0046] In order to make the matter which may absorb the oscillation wavelength of laser light in a resin particle contain in order to perform effectively heating welding of the self-water-dispersion resin particle by these laser light, or to make easy visual inspection of the laser light drawing section, the photosensitive or thermosensitive coloring matter may be made to contain.

[0047] When the self-water-dispersion thermoplastics in this invention prints using the lithography plate which has the self-water-dispersion resin particle layer which the acid number becomes from the resin with which it comes to neutralize or more 50 some 280 or less synthetic resin [ at least ] (A) by the base (B) Although the usual printing is possible since deck watertight luminaire and alkali resistance of the resin particle thermal melting arrival layer which the image section made lipophilic improve by inking If pH of the dampening water to be used exceeds 9, since the adhesion of the thermal melting arrival resin of the image section and a base will fall and LIFE of printing will become short, it is desirable to use and print with a pH of nine or less dampening water.

[0048]

[Embodiment of the Invention] It is as follows, when the case where the gestalt of suitable operation of this invention is manufactured by the phase inversion emulsifying method is made into an example and it explains.

[0049] After the acid number dissolved or less [ 50 or more ] in 280 and glass transition temperature dissolves synthetic resin 50 degrees C or more and the ionomer resin of the structure in which some synthetic resin carried out intermolecular bridge formation and which it unified through polyvalent metal ion especially preferably in an organic solvent, the alcoholic amine beyond 60 mol % of the acid radical of synthetic resin is mixed further.

[0050] It emulsifies by mixing the aqueous medium of the excessive amount which contains a glycerol in this resin solution as a particle adherent, the diameter resin particle of a large drop is removed by filter filtration, centrifugal separation, etc., and the water dispersion of a self-water-dispersion resin particle is obtained.

[0051] In order to remove spreading, superfluous water, and a low-boiling point organic solvent for the above-mentioned dispersion liquid to the aluminum plate with which the obtained self-moisture powder solution is given to graining and anodizing on the front face and to protect a printing plate, it covers with a PET film and considers as a printing plate.

[0052] A PET film is removed, on an aluminum plate, self-water-dispersion resin particles weld and they engrave by carrying out a temperature up with laser light to the temperature which carries out oleophilic resinification.

[0053] It prints using the usual offset press using with a pH of nine or less dampening water, without developing a printing plate [finishing / the above-mentioned platemaking].

[0054]

[Example] Next, an example and the example of a comparison are given and this invention is explained still more concretely. In addition, the "section" in the following examples expresses the "weight section."

[0055] (Example 1)

The styrene acrylic-acid-resin 20 section (styrene / acrylic acid / 2-ethylhexyl acrylate =80/10/10;)

Acid-number 82 and glass transition temperature of 70 degrees C

Triethanolamine The 3.1 sections (about 70% of neutralization indices of resin)

Methyl ethyl ketone 20 section isopropyl alcohol The ten sections [0056] Each above-mentioned component was added, it dissolved, and the synthetic-resin solution was obtained. Stirring this synthetic-resin solution, the mixed liquor of the glycerol 3 section and the ion-exchange-water 125 section was dropped at the rate of 5ml/m, and it considered as the resin emulsification object, and filtered using 0.5-micrometer filter, and the coating was obtained. The particle size of the obtained self-water-dispersion resin particle was 95nm.

[0057] The coat of the obtained coating was carried out to the aluminum plate for PS plates which it grained, and after being fully air-dry at 40 degrees C, it covered with the PET film and considered as the printing plate.

[0058] Although printed to paper of fine quality with the offset press (the HAMADA PRINTING PRESS make, dampening water pH=8.5), without removing the PET film of a printing plate and developing negatives by forming a thermal melting arrival image in a printing plate by the printer of semiconductor laser component loading, even if it passed over the 20,000 sections, there is no character dirt and the image section was also printed vividly.

[0059] (Example 2)

Styrene acrylic acid resin The 20 sections (styrene / acrylic-acid / methacrylic acid =77/10/13; acid-number 158 and glass transition temperature of 107 degrees C)

Tris acetylacetonate aluminum The 1.8 sections (30% considerable amount of rates of bridge formation)

Triethanolamine The 5.9 sections (70% considerable amount of neutralization indices)

Methyl ethyl ketone 30 section isopropyl alcohol The 20 sections [0060] The synthetic-resin solution was obtained having added each above-mentioned component, and dissolving and stirring. After having dropped the mixed liquor of the ion-exchange-water 200 section and the glycerol 5 section at this synthetic-resin solution at the rate of 5ml/m, considering as the resin emulsification object and removing a methyl ethyl ketone and isopropyl alcohol at 40 degrees C using a rotary evaporator, it filtered using 0.1-micrometer filter and considered as the coating. The particle size of the obtained self-water-dispersion resin particle was 23nm.

[0061] The coat of the obtained coating was carried out to the aluminum plate for PS plates which it grained, after being fully air-dry at 40 degrees C, reduced pressure drying was carried out further, and it covered with the PET film and considered as the printing plate.

[0062] Although printed to paper of fine quality with the offset press (the HAMADA PRINTING PRESS make, dampening water pH=8.5), without removing the PET film of a printing plate and developing negatives by forming a thermal melting arrival image in a printing plate by the printer of semiconductor laser component loading, even if it passed over the 30,000 sections, there is no character dirt and the image section was also printed vividly.

[0063] (Example 3)

Styrene acrylic acid resin The 20 sections (styrene / acrylic-acid / methacrylic acid =77/10/13; acid-number 158 and glass transition temperature of 107 degrees C)

Triethanolamine The 8.4 sections (about 100% of neutralization indices of resin)

Methyl ethyl ketone 20 section isopropyl alcohol The ten sections [0064] Each above-mentioned component was added, it dissolved, and the synthetic-resin solution was obtained. Stirring this synthetic-resin solution, the mixed liquor of the glycerol 3 section and the ion-exchange-water 125 section was dropped at the rate of 5ml/m, and it considered as the resin emulsification object, and filtered using 0.1-micrometer filter, and the coating was obtained. The particle size of the obtained self-water-dispersion resin particle was 39nm.

[0065] The coat of the obtained coating was carried out to the aluminum plate for PS plates which it grained, and after being fully air-dry at 40 degrees C, it covered with the PET film and considered as the printing plate.

[0066] Although printed to paper of fine quality with the offset press (the HAMADA PRINTING PRESS make, dampening water pH=8.5), without removing the PET film of a printing plate and developing negatives by forming a thermal melting arrival image in a printing plate by the printer of semiconductor laser component loading, even if it passed over the 20,000 sections, there is no character dirt and the image section was also printed vividly.

[0067]

[Effect of the Invention] the base front face of the hydrophilic property of this invention — heat — lipophilic — in

the signal from a computer, the printing approach using the lithography plate and it by which the self-water-dispersion thermoplastics particle layer [-izing / the layer ] is formed can be engraved direct, without performing development actuation, is excellent in the ink impression stability in the image section with high resolution, and offers printed matter without the ink dirt of the non-image section.

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[Translation done.]



(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平9-127683

(43) 公開日 平成9年(1997)5月16日

(51) Int.Cl. <sup>6</sup>	識別記号	序内整理番号	F I	技術表示箇所
G 0 3 F 7/00	5 0 3		G 0 3 F 7/00	5 0 3
B 4 1 M 1/06			B 4 1 M 1/06	

審査請求 未請求 請求項の数14 O L (全 7 頁)

(21) 出願番号 特願平7-283247

(22) 出願日 平成7年(1995)10月31日

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(54) 【発明の名称】 平版印刷版及び印刷方法

(57) 【要約】

【課題】 熱記録手段を用いて、現像操作を行うことなく直接製版可能で、高解像度で画像部でのインキ着肉安定性に優れ、非画像部のインキ汚れのない印刷物を提供する。

【解決手段】 親水性の基体表面に熱により親油化可能な自己水分散性熱可塑性樹脂粒子層が形成されていることを特徴とする平版印刷板。当該平版印刷板に、熱エネルギーを与えて所望の位置の前記粒子を親油化し熱融着画像を形成させ、浸し水を用いて前記熱融着画像にインキを着肉し被記録体にそれを転写することにより印刷を行う印刷方法。

【特許請求の範囲】

【請求項1】 親水性の基体表面に熱により親油化可能な自己水分散性熱可塑性樹脂粒子層が形成されていることを特徴とする平版印刷板。

【請求項2】 親水性の基体がアルミニウム板であることを特徴とする請求項1記載の平版印刷板。

【請求項3】 自己水分散性熱可塑性樹脂が、酸価が50以上280以下の合成樹脂(A)の少なくとも一部が塩基(B)で中和されてなる樹脂であることを特徴とする請求項1又は2記載の平版印刷板。

【請求項4】 合成樹脂(A)のガラス転移温度が50℃以上である請求項3記載の平版印刷板。

【請求項5】 合成樹脂(A)の酸基の60モル%以上が塩基(B)で中和されている自己水分散性樹脂であることを特徴とする請求項3又は4記載の平版印刷板。

【請求項6】 合成樹脂(A)が、スチレン、置換スチレン、(メタ)アクリル酸エステルからなる群から選ばれる少なくとも一つのモノマーと、(メタ)アクリル酸との共重合体である請求項3、4又は5記載の平版印刷板。

【請求項7】 自己水分散性熱可塑性樹脂が、合成樹脂(A)中の酸価を与える官能基全量の少なくとも一部が、多価金属イオン(C)を介して分子間架橋し一体化した構造のアイオノマー樹脂(I)であることを特徴とする請求項3、4又は5記載の平版印刷板。

【請求項8】 塩基(B)が、アルコールアミンである請求項3、4、5、6又は7記載の平版印刷板。

【請求項9】 塩基(B)が、トリエタノールアミンである請求項8記載の平版印刷板。

【請求項10】 自己水分散性熱可塑性樹脂粒子層に粒子付着防止剤(D)を含有する請求項1又は2記載の平版印刷板。

【請求項11】 粒子付着防止剤(D)が多価アルコールであることを特徴とする請求項10記載の平版印刷板。

【請求項12】 粒子付着防止剤(D)がグリセリンであることを特徴とする請求項11記載の平版印刷板。

【請求項13】 親水性の基体表面上の自己水分散性熱可塑性樹脂粒子層の上に更に剥離可能な乾燥防止用フィルムが形成されていることを特徴とする請求項8、9、11又は12記載の平版印刷板。

【請求項14】 親水性の基体表面に熱により親油化可能な自己水分散性熱可塑性樹脂粒子層が形成されている平版印刷板に、熱エネルギーを与えて所望の位置の前記粒子を親油化し熱融着画像を形成させ、浸し水を用いて前記熱融着画像にインキを着肉し被記録体にそれを転写することにより印刷を行うことを特徴とする印刷方法。

【発明の詳細な説明】

【0001】

【発明が属する技術分野】 本発明は平版印刷のための印

刷版に関し、詳しくは、ヒートモードのレーザー光で直接描画する事により選択的にインキの着肉可能な画像部を形成し、かつ現像操作を行わずにそのまま印刷可能な平版印刷版に関する。

【0002】

【従来の技術】 従来の製版システムは版下からネガあるいはポジのフィルムを作成し、感光性ポリマーを塗布したPS板に焼き付けて、さらに現像を行って製版を行うという非常に手間のかかるものであった。近年製版のデジタル化が急速に進み、コンピューターからの電気信号を直接製版に結びつける手段が提案されている。

【0003】 具体的には、コンピューターからの電気信号をレーザー光に変換し、感光性ポリマーに焼き付けた後に現像を行って製版化する方法が一般的であるが、依然として現像工程が必要である。また直接版上に画像形成材料をマテリアルトランスファーして製版する方法としてインクジェット記録や電子写真方式が提案されているが、画像部の再現安定性や解像度に欠点を有している。

【0004】 その他の方法として、特開昭62-1587号公報ではマイクロカプセル化された親油物質を画像受理層とし、インパクト方式のプリンターでマイクロカプセル層を破壊して画像部を形成する直描型オフセット印刷用原版が提案されているが、マイクロカプセルの粒子径が大きく、また衝撃によりカプセルを破壊するため画像部の広がり避けられず、得られる印刷物の解像度が基本的に低く、さらに版上で非画像部のカプセルの破壊による印刷汚れを生じ易いという欠点を有している。

【0005】 印刷画像の再現安定性や高解像度を達成し、かつ現像操作を行うことなく製版を行う手段として、サーマルヘッドやレーザー光を用いたダイレクト製版が種々提案されている。例えば、特開昭49-118501号公報は、親油性樹脂を成分とする物体の表面を化成処理して親水性層を形成し、その親水性層をレーザー光により選択的に除去して画像部を形成させる方法であるが、この方法ではエネルギーを多大に消費し、製版速度も遅く、ポリマー屑や燃え殻の発生のため解像度が低いという欠点を有している。

【0006】 特開昭51-63704号公報は、非感光性化合物よりなる親水性ポリマー層で覆われた版材をレーザー光で照射する事により、照射部分が硬化し疎水性あるいは親油性となり、インキを吸収するように変化させるものであるが、この方法では画像部を強固にかつ均一に変化させることは困難であり、印刷中に非画像部を構成する水溶性ポリマーが溶出して印刷汚れが発生しやすいという欠点がある。

【0007】 特開平3-108588号公報では熱溶融物質を顔料でマイクロカプセル化された熱溶融物質を支持体に塗布し、加熱部を親油性に変化させてインキの着肉を行う方法が提案されているが、マイクロカプセルの

粒子径が大きく得られる印刷物の解像度が基本的に低く、版上でカプセルの破壊や壁を通して親油性の熱溶融物質が支持体に付着しやすく印刷汚れを生じ易いという欠点を有している。

【0008】特公平6-71787号公報は親油性ポリマーよりなる版材の表面にスルホン酸基を導入して非画像部を形成し、特定のエネルギー密度を有するレーザー光の照射により表面のスルホン酸基を選択的に除去して画像部を形成する方法であるが、スルホン酸基処理をされた表面下部の親油性ポリマー層の部分露出により、印刷汚れが生じ易いという欠点を有していた。

【0009】特開平7-1849号公報、特開平7-1850号公報では熱により画像部に転換するマイクロカプセル化された親油性成分と親水性バインダーポリマーとを含有する親水層及び支持体とから構成され、親水性バインダーポリマーが三次元架橋されていて、かつマイクロカプセル中の親油成分とカプセルの破壊後化学結合する様に工夫された感熱平版印刷板が提案されているが、マイクロカプセルの粒子径が大きく得られる印刷物の解像度が基本的に低く、また基本的に親水性ポリマーと支持体との密着性が十分でなく、また親油成分と親水性ポリマーの境界が明確でないため、印刷汚れや解像度の低下という問題を有している。

【0010】

【発明が解決しようとする課題】本発明が解決しようとする課題は、コンピューターからの信号を直接製版可能で、高解像度で画像部でのインキ着肉安定性に優れ、非画像部のインキ汚れのない、平版印刷板と安定した印刷が可能な印刷方法を提供することにある。

【0011】

【課題を解決するための手段】本発明者等は、上記の課題を解決するために鋭意研究を重ねた結果、本発明を解決するに至った。

【0012】即ち、本発明は、親水性の基体表面、好ましくはアルミニウム板表面に形成された熱により親油化可能な自己水分散性熱可塑性樹脂粒子層が形成されているダイレクト製版可能な平版印刷板を提供する。

【0013】また、親水性の基体表面に熱により親油化可能な自己水分散性熱可塑性樹脂粒子層が形成されている平版印刷板に、熱エネルギーを与えて所望の位置の前記粒子を親油化し熱融着画像を形成させ、浸し水を用いて前記熱融着画像にインキを着肉し被記録体にそれを転写することにより印刷を行うことを特徴とする印刷方法を提供する。

【0014】前記平版印刷板の自己水分散性熱可塑性樹脂は酸価が50以上280以下、好ましくはガラス転移温度が50℃以上の合成樹脂(A)の少なくとも一部がアルコールアミン等の塩基(B)で中和されてなる自己水分散性樹脂、特に好ましくは合成樹脂(A)の酸価を与える官能基全量の少なくとも一部が、多価金属イオン

(C)を介して分子間架橋し一体化した構造のアイオノマー樹脂(I)である平版印刷板を提供する。

【0015】前記平版印刷板の自己水分散性熱可塑性樹脂粒子層に多価アルコール等の粒子付着防止剤(D)を含有し、さらに好ましくは親水性の基体表面上の自己水分散性熱可塑性樹脂粒子層の上に、剥離可能な乾燥防止用フィルムが形成されている平版印刷板を提供する。

【0016】本発明の印刷板は、基体表面に形成された自己水分散性熱可塑性樹脂粒子層を有するものであり、印刷板に選択的にエネルギーを加えて該樹脂粒子を融着及び親油化した後に、融着樹脂粒子層にインキングを施し、さらに被記録体にインキを転写して印刷画像を形成するいわゆる平版印刷に用いる。

【0017】印刷板に与えるエネルギー形態としては照射により自己水分散性熱可塑性樹脂粒子を選択的に融着しうるものであれば特に制限は無いが熱エネルギーが簡易で効率的であり、熱源としてはサーマルヘッドやレーザー光等があるが、非接触で微細パターンを直接描画可能なレーザー光が最も好ましい。解像度の点で該樹脂粒子の粒子径は小さいほどよく、1μm以下さらに好ましくは0.1μm以下が好ましい。

【0018】一方、印刷板の未描画部分は親水性に富んでいて、そのままあるいは湿し水の付与によって印刷インキの着肉を防止し、非画像部とすることができる。さらに印刷が進むと未融着の自己水分散性熱可塑性樹脂粒子は基体表面から容易に離脱し、基体本来の親水効果によって従来の平版印刷板と同様な印刷安定性が得られる。

【0019】以上のように本発明の印刷板を用いると製版における現像操作が不要になるが、必要に応じて、水等を用いて予め版の現像を行って非画像部の該樹脂粒子を事前に除去しておいてから用いるようにしても良い。

【0020】本発明の平版印刷板の目的は、自己水分散性熱可塑性樹脂粒子層の熱溶融画像部の解像度・基体との密着性・インキ耐油性と未溶融非画像部の樹脂粒子同士の付着防止・親水性保持・樹脂粒子の基体からの離脱を容易にすることである。

【0021】即ち、本発明の平版印刷板は、親水性の基体表面に熱により親油化可能な自己水分散性熱可塑性樹脂粒子層が形成されていることを特徴としており、親水性基体は紙・プラスチック・金属等限定はないが、コーティング処理された紙、コロナ放電等の処理によって表面を親水性化されたプラスチックシート、好ましくはアルミニウム板、さらに好ましくはその表面が砂目立てや陽極酸化処理等の表面処理が施されていることが好ましい。

【0022】基体表面の自己水分散性熱可塑性樹脂粒子層は、該樹脂粒子の水分散液を基体表面に塗布乾燥して得られるが、一般の樹脂粒子ではその乾燥塗膜は粒子同士が部分的に融合して皮膜を形成するために、レーザー

光の未融着部分の親水性が不十分となり、さらに基体表面からの樹脂粒子層の離脱が行われず、非画像部へのインキの着肉が生じやすくなる。

【0023】自己水分散性樹脂としては酸価を有している合成樹脂と塩基性物質との塩や、水酸基等の親水基を置換基として有するものがあるが、水分散性樹脂粒子の微粒子化と、粒子の溶解・膨潤を防ぎながらかつ粒子に大きな親水性を付与するために、樹脂としては酸価が50以上280以下の合成樹脂(A)の少なくとも一部が塩基(B)で中和されてなる自己水分散性樹脂であることが好ましい。特に該樹脂粒子同士の融合を防止するには、樹脂のガラス転移温度が50℃以上が好ましく、さらに好ましくは70℃以上のガラス転移温度が良い。

【0024】画像部の解像性を上げるためより樹脂粒子の粒子径を小さくし、非画像部の未融着の樹脂粒子の親水性を高めて非画像部のインキ汚れを小さくするためには、合成樹脂(A)の酸基の60モル%以上が塩基

(B)で中和されていることが好ましい。合成樹脂に酸価を与えるアニオン性官能基はカルボキシル基、スルホン酸基、スルフィン酸基等特に限定されるものではないが、カルボキシル基は一般的で良好な自己水分散性熱可塑性樹脂粒子を与える。

【0025】自己水分散性樹脂粒子の樹脂の種類は特に制限はないが、樹脂の粒子化、画像部の皮膜強度、非画像部の親水性等を満足するものとして、スチレンあるいは $\alpha$ -メチルスチレンのような置換スチレン、アクリル酸メチルエステル、アクリル酸エチルエステル、アクリル酸ブチルエステル、アクリル酸2-エチルヘキシルエステル等のアクリル酸エステル、メタクリル酸メチルエステル、メタクリル酸エチルエステル、メタクリル酸ブチルエステル、メタクリル酸2-エチルヘキシル等のメタクリル酸エステルから選ばれる少なくとも一つ以上のモノマー単位と、アクリル酸、メタクリル酸から選ばれる少なくとも一つ以上のモノマー単位を含む共重合体が好ましく、また特に樹脂の分子量範囲について制限はないが1000以上10万以下の分子量のものがより好ましい。

【0026】前記樹脂の基体表面への密着性、画像部の耐摩耗性・耐油性・耐アルカリ性、非画像部の粒子同士の融着防止をさらに改善する手段として、自己水分散性熱可塑性樹脂が、合成樹脂(A)中の酸価を与える官能基全量の少なくとも一部が、多価金属イオン(C)を介して分子間架橋し一体化した構造のアイオノマー樹脂(1)であることが好ましい。

【0027】アイオノマー樹脂とは永久網目構造を持つ永久ゲルを形成する共有結合性架橋と異なり、可逆的架橋からなる網目構造を持つ可逆ゲルを形成する多価金属イオンとアニオン性基のイオニックな結合によるキレート樹脂であり、該水分散液から得られる樹脂粒子及び熱融着樹脂皮膜は極めて強靱で弾性に富んでいて、基体アル

ミニウム板との密着性が優れている。可逆的架橋とは即ちイオン結合エネルギーが共有結合エネルギーと比較して小さいことから、架橋率が高くて良好な熱可塑性を示すということである。

【0028】アイオノマー樹脂に使用する多価金属イオンの価数は2以上であればどれでも良いが、好ましくは2または3であり、特に好ましくはカルシウムイオン、バリウムイオン、マグネシウムイオン、亜鉛イオン、アルミニウムイオンから少なくとも一つ以上選ばれたものから得られる樹脂粒子が無色で、毒性も少なく、良好な強靱でかつ良好な熱可塑性を示す。これらの多価金属イオンによる樹脂の架橋は、好ましくはアニオン性の官能基の1%から30%に相当する量の多価金属イオンで架橋される場合、合成樹脂のゲル化が少なく安定したアイオノマー樹脂水分散液が得られ、樹脂粒子の熱流動特性の低下も少ない。

【0029】多価金属イオンは金属あるいは可溶性多価金属塩として樹脂溶液に添加され、多価金属のカルボン酸塩やアセチルアセトン、アセト酢酸エステル塩等の配位子と多価金属の金属キレートから選ばれるものは入手のし易さや有機溶剤に対する溶解性の点で好ましい。

【0030】これら可溶性金属塩を合成樹脂溶液に入れると架橋により樹脂の溶解性が低下し、ゲル化や樹脂乳化物の大粒径化が生じるが、この時は液温を上げるか、アセチルアセトンやアセト酢酸エステルのような揮発性のキレート剤を過剰に加えることによりゲル化を防止し、微粒径の樹脂乳化物が得られる。

【0031】自己水分散性を前記合成樹脂(A)に付与するための塩基(B)は該樹脂粒子の親水性とレーザー光照射による熱融着及び融着樹脂皮膜の親油性に大きな影響を与える。塩基(B)がアルカリ金属の場合はレーザー光照射による熱融着皮膜の親油化は十分ではなく画像部のインキ着肉が不十分であり、アンモニアのように揮発性が高すぎると画像部のインキ着肉は十分であるが非画像部の該樹脂粒子が親油化して版のインキ汚れを生じ易い。好ましい塩基(B)としては蒸気圧の低いアミン類、好ましくはアルコールアミン、さらに好ましくはトリエタノールアミンが好ましい。

【0032】本発明において、さらに版のインキ汚れを防止するには、自己水分散性熱可塑性樹脂粒子層に水性樹脂や親水性無機微粒子粒子や多価アルコール等の粒子付着防止剤を含ませることができ、好ましくは多価アルコール、特に多価アルコールがグリセリンの場合は樹脂粒子が基体表面に残存していても非画像部へのインキ着肉を効果的に防ぎ、かつ親水性基体表面からの樹脂粒子の離脱を容易にして従来の印刷板と同等以上の版のインキ汚れ防止が可能となる。

【0033】親水性の基体表面上の自己水分散性熱可塑性樹脂粒子層に前記液状の塩基や粒子付着防止剤を含む場合には、版の保存安定性を高めるために剥離可能な乾

燥防止用フィルムが該樹脂粒子層上に形成されていることが望ましい。

【0034】本発明の自己水分散性熱可塑性樹脂粒子は、既知の乳化重合法や親油性ポリマーを乳化剤で強制的に乳化したものと異なり、本質的に親水性を有する自己乳化性樹脂粒子を容易に得ることができる転相乳化法によって得られる。

【0035】具体的には、第一段階として自己水分散性樹脂を有機溶媒に溶解した後更に所定量の中和塩基を混合する。第二段階として、第一段階で得られた樹脂溶液に過剰量の水性媒体を混合させることにより乳化を行い、樹脂粒子の水分散液を得る。

【0036】必要に応じて第三段階として、樹脂粒子分散液の分散安定性を高めるために、第一段階で用いた有機溶媒を除去する脱溶媒工程を入れてもよい。また第二または第三段階の工程が終了した後、フィルターろ過や遠心分離等で大粒径樹脂粒子を除去する工程を行うことが好ましい。

【0037】第一段階において合成樹脂（A）を溶解する有機溶媒はアセトン、ジメチルケトン、メチルエチルケトン等のケトン系溶媒、メタノール、エタノール、イソプロピルアルコール等のアルコール系溶媒、クロロホルム、塩化メチレン等の塩素系溶媒、ベンゼン、トルエン等の芳香族系溶媒、酢酸エチルエステル等のエステル系溶媒、エチレングリコールモノメチルエーテル、エチレングリコールジメチルエーテル等のグリコールエーテル系溶媒、アミド類等樹脂を溶解させるものであれば使用可能であるが、樹脂成分がアクリル系樹脂の場合にはケトン系溶媒とアルコール系溶媒から選ばれる少なくとも1種類以上の組み合わせが良い。

【0038】かかる有機溶媒の使用量は、本発明における効果を達成すれば特に規定されないが、合成樹脂／該有機溶媒の重量比が1/1～1/20となるような量が好ましい。

【0039】上記合成樹脂溶液には、添加剤として、必要に応じて分散剤、可塑剤、酸化防止剤、紫外線吸収剤や、照射するエネルギーを効率よく吸収するためのエネルギー吸収剤等を加えておく事もできる。

【0040】上記合成樹脂溶液と混合される水性媒体は、夾雑物や重金属類による影響を回避するためにイオン交換水以上のグレードの水が好ましい。

【0041】また自己水分散性樹脂粒子層には、粒子付着防止剤（D）を併用するのが好ましく、粒子付着防止剤（D）としてはエチレングリコール、ジエチレングリコール、ポリエチレングリコール、グリセリン等の多価アルコール類、コロイダルシリカ等の無機の微粒子、界面活性剤等があり、これらに限定されるものではないが、特に本発明においてはグリセリンが粒子同士の融着防止に効果的である。

【0042】これら粒子付着防止剤（D）は液状のもの

については乳化に用いる前記水性媒体中に加えておいても良いが、該樹脂粒子の水分散液に後添加しても良く、それらの添加量は、通常、該樹脂粒子100重量部に対して1～500重量部の範囲かである。

【0043】得られた自己水分散性樹脂粒子分散溶液は、アルミニウム等の親水性基体に、既知の方法で塗布、過剰の水や低沸点の有機溶剤を除去し印刷板とする。得られた自己水分散性樹脂粒子層の個々の粒子は、いわゆる粉体粒子とは異なり印刷板上から容易に離脱することなく、見かけは通常の樹脂層と変わらない。自己水分散性樹脂粒子溶液には添加剤として、前記粒子付着剤、防腐剤、レーザー光により活性化可能な粒子架橋剤等を添加してもよい。

【0044】塩基としてアルコールアミン、粒子付着防止剤としてグリセリンのような溶剤を使用する場合で、長期間印刷板の保存をする場合には、これら溶剤の蒸発に伴う粒子同士の付着を防止し、印刷板の保護を行うためPET等の剥離可能なフィルムで覆うことが好ましい。

【0045】本発明の平版印刷板の製版に用いるレーザー光源としては、自己水分散性樹脂粒子同士が融着する温度まで昇温可能で、かつ自己水分散性樹脂粒子層の食刻が生じない程度にコントロールされていればよく、具体的には半導体レーザー（発振波長780nm/840nm）、炭酸ガスレーザー（同10.6μm）、YAGレーザー（同532・1060nm）・エキシマレーザー（同193・308・351nm）アルゴンレーザー（同488nm）等がある。

【0046】これらレーザー光による自己水分散性樹脂粒子の加熱融着を効果的に行うために、樹脂粒子中にレーザー光の発振波長を吸収しうる物質を含有させたり、レーザー光描画部の目視確認を容易にするために、感光性あるいは感熱性の発色物質を含有させても良い。

【0047】本発明における自己水分散性熱可塑性樹脂が、酸価が50以上280以下の合成樹脂（A）の少なくとも一部が塩基（B）で中和されてなる樹脂からなる自己水分散性樹脂粒子層を有する平版印刷板を用いて印刷を行う場合には、画像部の親油化した樹脂粒子熱融着層はインキングによって耐水・耐アルカリ性が向上するため通常の印刷が可能であるが、使用する湿し水のpHが9を越えると、画像部の熱融着樹脂と基体の密着性が低下し印刷のライフが短くなるために、pH9以下の湿し水を用いて印刷することが好ましい。

【0048】

【発明の実施の形態】本発明の好適な実施の形態を転相乳化法によって製造する場合を例にして説明すると次の通りである。

【0049】酸価が50以上280以下、ガラス転移温度が50℃以上の合成樹脂、特に好ましくは合成樹脂の一部が、多価金属イオンを介して分子間架橋し一体化し

た構造のアイオノマー樹脂を有機溶媒に溶解した後、更に合成樹脂の酸基の60モル%以上のアルコールアミンを混合する。

【0050】この樹脂溶液に、粒子付着防止剤としてグリセリンを含む過剰量の水性媒体を混合させることにより乳化を行い、フィルターろ過や遠心分離等で大粒径樹脂粒子を除去して自己水分散性樹脂粒子の水分散液を得る。

【0051】得られた自己水分散溶液を表面が砂目立てや陽極酸化処理が施されているアルミニウム板に上記分散液を塗布、過剰の水及び低沸点有機溶剤を除去し、印刷板の保護を行うためPETフィルムで覆い印刷板とす

スチレンアクリル酸樹脂

(スチレン/アクリル酸/アクリル酸2-エチルヘキシル=80/10/10;

酸価82・ガラス転移温度70℃)

トリエタノールアミン

メチルエチルケトン

イソプロピルアルコール

【0056】上記各成分を加えて溶解し、合成樹脂溶液を得た。この合成樹脂溶液を攪拌しながら、グリセリン3部とイオン交換水125部の混合液を毎分5mlの速度で滴下して樹脂乳化物とし、0.5μmフィルターを用いてろ過を行い塗料を得た。得られた自己水分散性樹脂粒子の粒径は95nmであった。

【0057】得られた塗料を砂目立てされたPS版用アルミニウムプレートにコートし、40℃で十分に風乾し

スチレンアクリル酸樹脂

(スチレン/アクリル酸/メタアクリル酸=77/10/13; 酸価158・ガラス転移温度107℃)

トリスアセチルアセトナトアルミニウム

)

トリエタノールアミン

)

メチルエチルケトン

イソプロピルアルコール

【0060】上記各成分を加えて溶解し、攪拌しながら合成樹脂溶液を得た。この合成樹脂溶液にイオン交換水200部、グリセリン5部の混合液を毎分5mlの速度で滴下して樹脂乳化物とし、ロータリーエバポレーターを用いて40℃でメチルエチルケトンとイソプロピルアルコールを除去した後、0.1μmフィルターを用いてろ過を行い塗料とした。得られた自己水分散性樹脂粒子の粒径は23nmであった。

【0061】得られた塗料を砂目立てされたPS版用アルミニウムプレートにコートし、40℃で十分に風乾し

スチレンアクリル酸樹脂

(スチレン/アクリル酸/メタアクリル酸=77/10/13; 酸価158・ガラス転移温度107℃)

トリエタノールアミン

メチルエチルケトン

る。

【0052】PETフィルムを剥がし、アルミ板上で自己水分散性樹脂粒子同士が融着し、親油性樹脂化する温度までレーザー光で昇温し、製版を行う。

【0053】上記製版済みの印刷板を現像することなく、pH9以下の湿し水を用いて通常のオフセット印刷機を用いて印刷をする。

【0054】

【実施例】次に実施例及び比較例を挙げて本発明を更に具体的に説明する。尚、以下の実施例中における「部」は『重量部』を表わす。

【0055】(実施例1)

20部

3. 1部(樹脂の中和率70%相当)

20部

10部

た後PETフィルムでカバーを行い印刷板とした。

【0058】印刷板のPETフィルムを剥がし、半導体レーザー素子搭載の印字装置で印刷板に熱融着画像を形成し、現像を行わずにオフセット印刷機(ハマダ印刷機械製、湿し水pH=8.5)で上質紙に印刷を行ったが、2万部を過ぎても字汚れはなく、画像部も鮮明に印刷された。

【0059】(実施例2)

20部

1. 8部(架橋率30%相当量)

5. 9部(中和率70%相当量)

30部

20部

た後更に減圧乾燥し、PETフィルムでカバーを行い印刷板とした。

【0062】印刷板のPETフィルムを剥がし、半導体レーザー素子搭載の印字装置で印刷板に熱融着画像を形成し、現像を行わずにオフセット印刷機(ハマダ印刷機械製、湿し水pH=8.5)で上質紙に印刷を行ったが、3万部を過ぎても字汚れはなく、画像部も鮮明に印刷された。

【0063】(実施例3)

20部

8. 4部(樹脂の中和率100%相当)

20部

#### イソプロピルアルコール

【0064】上記各成分を加えて溶解し、合成樹脂溶液を得た。この合成樹脂溶液を攪拌しながら、グリセリン3部とイオン交換水125部の混合液を毎分5mlの速度で滴下して樹脂乳化物とし、0.1 $\mu$ mフィルターを用いてろ過を行い塗料を得た。得られた自己水分散性樹脂粒子の粒径は39nmであった。

【0065】得られた塗料を砂目立てされたPS版用アルミニウムプレートにコートし、40℃で十分に風乾した後PETフィルムでカバーを行い印刷板とした。

【0066】印刷板のPETフィルムを剥がし、半導体レーザー素子搭載の印字装置で印刷板に熱融着画像を形

#### 10部

成し、現像を行わずにオフセット印刷機（ハマダ印刷機械製、湿し水pH=8.5）で上質紙に印刷を行ったが、2万部を過ぎても字汚れはなく、画像部も鮮明に印刷された。

#### 【0067】

【発明の効果】本発明の親水性の基体表面に熱により親油化可能な自己水分散性熱可塑性樹脂粒子層が形成されている平版印刷板及びそれを用いた印刷方法は、コンピューターからの信号を現像操作を行うことなく直接製版可能で、高解像度で画像部でのインキ着肉安定性に優れ、非画像部のインキ汚れのない印刷物を提供する。